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TITLE OF INVENTION

POLYAMIDE COMPOSITION, STABILIZED WITH COPPER COMPLEXES AND ORGANIC HALOGEN COMPOUNDS

APPLICANT(S) FOR DO/EO/US

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Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (24) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31)
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
 - a. ☐ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☒ has been communicated by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
- ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☒ is attached hereto.
 - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
- ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ have been communicated by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired
 - d. ☒ have not been made and will not be made.
- ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
- ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
- ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).
11. ☒ A copy of the International Preliminary Examination Report (PCT/IPEA/409)
12. ☒ A copy of the International Search Report (PCT/ISA/210).

Items 13 to 20 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included
15. ☐ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter
19. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
20. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
21. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
22. ☒ Certificate of Mailing by Express Mail
23. ☒ Other items or information:

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Polyamide composition, stabilized with copper complexes and organic halogen compounds

The present invention relates to stabilized polyamide compositions.

Polymers are degraded easily when heated by oxidation, which leads to embrittlement of the material and to mechanical failure of the products produced therefrom. Therefore particular chemical compounds are added which can delay the time of embrittlement with different activity. These so-called antioxidants are mostly built on the basis of phenyl derivatives, amine derivatives or phosphorous derivatives. Specific variants of antioxidants are employed with polyamides. One in particular active class of compounds, which does not have any activity with other polymers, are the so-called copper stabilizers.

These types of stabilizing systems are long known and are used widely for the preparation of polyamides, for examples for polyamide filaments which are used for the production of tyre cord and for polyamide extrusion molding parts for technical employment, in particular in the area of technical engineering (automobiles) and the electronic industry (switches, printed circuit boards).

These copper stabilizers usually consist of two components, a mixture of copper compounds and specific halogen salts. The typical copper compounds are copper (I) halides and copper salts, such as copper acetate, copper sulfate or copper stearate and copper complexes, such as copper acetylacetonate. In order to be effective as antioxidants, halogen compounds must be added in a large surplus. Used in this respect are in particular potassium iodide and also potassium bromide. The employed amount is typically chosen so that the molar ratio of copper to halogen is 1:5-15. The recommended amount is generally 30 to 200 ppm copper and accordingly 150 to 3,000 ppm halogen.

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These copper stabilizers lead to stabilized polyamide products which can be subjected to thermal stress from 150 to 180 °C for a short period of time, without degradation by ambient oxygen to embrittlement. The durability at 150 °C can be from 1,000 to 2,000 hours until the mechanical properties decrease to 50% of the initial value.

However, these commonly employed copper stabilizers do show some severe drawbacks.

Polyamides take up (conditioning) approximately 3% water. If the temperature changes water soluble components are extracted from the polyamide to the surface, which leads to the formation of scale. If copper halides, potassium halides or other soluble halides are employed these will be extracted to the surface and will form a hygroscopic scale which will react mostly acidic. Therefore the tracking resistance will decrease. With electric components this may lead to failure. If contact with metals is given the contact places will endure increased corrosion. Requirements of the electronic industry and the automobile industry regarding the question of tracking resistance are therefore difficult to fulfil.

When preparing stabilized polyamides it is important to make sure that the employed stabilizers are finely powdered and can be admixed with the polyamide very homogeneously. On problem associated therewith is usually the tendency of the usually employed components to agglomerate. The raw materials must therefore be ground very finely and must be protected against reagglomeration. The addition itself is, due to the minute amounts employed usually very difficult to control, therefore usually a master batch will be produced which will be added. Even then such a heterogeneous mixture of solid particles in a melt is never optimal, compared with the hypothetical case that the stabilizer itself would be meltable and could be dispersed homogeneously under working conditions. The crystalline particles of the stabilizer salts effect the physical properties of the polyamides negative, even if they are finely dispersed. This does not only result from possible inhomogeneity but also from the fact that fine particles act as crystallisation nuclei which result in a higher

crystallinity in polymers. This leads to negative side effects. The impact strength can for example decrease by 20 to 30%, compared with the initial value of the non-stabilized polyamide.

Copper compounds furthermore lead in polyamides after conditioning often to a bluish or greenish discoloration. Polyamides reinforced with fiber glass may furthermore show a brown coloration due to the formation of copper oxide, resulting from high sheer stress given during processing. In particular negative are variations of the discoloration during the production cycles, which will make the use of the produced materials for non-colored or colored products difficult. Therefore such polyamides are usually employed after black coloration.

Copper salt/halogen salt-stabilizers are often added during the polymerization as aqueous solution in order to optimise the dispersion. One drawback is however that this addition may lead to formation of scale of metallic copper or of copper oxide on the metal surface of the employed vessels and melt extruders. This may lead to variation in coloration and therefore to the discontinuation of the production. During spinning of filaments scale formation at the nozzle is often encountered which will lead to the discontinuation of the process.

Furthermore the durability of polyamides stabilized with conventional stabilizers at temperatures above 150 °C is not sufficient.

In view of these drawbacks several improvements were proposed.

DE-A-1237309, DE-A-1245591, DE-A-1259094 and NL-A-6501290 disclose the use of copper phosphine complexes for the stabilization of polyamides. These stabilizers are employed in view of the improved thermal stabilization. DE-A-1245591 and DE-A-1259094 disclose furthermore that the stabilizing activity of the copper phosphine complexes can be improved by addition of iodid salt.

These stabilizers are however still disadvantageous concerning tracking resistance, thermal stability at temperatures above 150 °C and stability against extraction.

It is therefore the object of the present invention to provide a stabilized polyamide composition which does not show the above named drawbacks.

This object is solved in accordance with the present invention by the provision of a stabilized polyamide composition, characterized in that as stabilizer at least one complex of copper and at least one organic halogen compound is contained.

Furthermore the present invention provides a process for the preparation of a stabilized polyamide composition, comprising the mixing of at least one copper complex and at least one organic halogen compound with at least one polyamide.

Furthermore the present invention provides a stabilized polyamide composition, characterized in that as stabilizer at least one copper complex with a phosphine compound and/or mercaptobenzimidazole compound is contained, which complex shows halogen-carbon-bonds.

It was found surprisingly that the stabilized polyamide composition in accordance with the present invention is able to avoid the drawbacks of the prior art. The drawbacks of the prior art, namely insufficient tracking resistance, insufficient stability at temperatures above 150 °C and undesired discoloration of stabilized products, do not occur with the stabilized polyamide compositions in accordance with the present invention or only to a neglectable extent.

In accordance with the present invention all typical polyamides may be employed. Polyamides are polymers showing recurrent carbon amide groups -CO-NH- in the polymer backbone. Polyamides are made from

- (a) amino carboxylic acids and their functional derivatives, for example lactames; or from
- (b) diamines and dicarboxylic acids or their functional derivatives.

By varying the monomer units polyamides are obtainable in a broad variety. The most common types are polyamide 6 from ϵ -caprolactam, polyamide 66 from hexamethylene diamine and adipic acid, polyamide 610 and 612, polyamide 11, polyamide 12, PACM-12 and polyamide 6-2-T and the aramides.

In accordance with the present invention however all further polyamides may be stabilized, for example copolyamides or block copolymers of polyamides and polyesters. It is furthermore possible to use blends of polyamides with other polymers.

In particular preferred are polyamide 6 and polyamide 66.

In accordance with the present invention all copper complexes may be used. Typical examples of complex ligands are triphenyl phosphines, mercaptobenzimidazole, EDTA, acetylacetonate, glycine, ethylenediamine, oxalate, diethylenetriamine, triethylene tetraamine, pyridine, diphosphone and dipyrityl.

These ligands may be employed singly or in combination for complex formation. The necessary synthesis are known to the skilled person or described in the literature. As usual these complexes may contain, in addition to the above-named ligands, furthermore typical inorganic ligands such as water, chloride, cyano etc.

Preferred are copper complexes with the ligands triphenylphosphine, mercaptobenzimidazole, acetylacetonate and glycine. In particular preferred are triphenylphosphine and mercaptobenzimidazole.

Preferred copper complexes used in accordance with the present invention are typically prepared by the reaction of copper (I) ions with phosphine or mercaptobenzimidazole compounds. For example these complexes can be

obtained by reacting triphenyl phosphine with copper (I) halide suspended in chloroform (G.Kosta, E. Resienhofer and L.Stafani, J. Inorg. Nukl. chem 27 (19565) 2581). It is however possible to react copper (II) compounds with triphenyl phosphine under reductive conditions, in order to obtain the copper (I) addition compounds (FU Jardine. L. Rule, A.G. Vorhei, J. Chem. Soc. (Q) 238-241 (1970).

The complexes employed in accordance with the present invention may however be furthermore prepared by any suitable process. Useable copper compounds for the preparation of these complexes are copper (I) or (II) salts of halogen acids or cyan acids or copper salts of the aliphatic carboxylic acids. Examples for suitable copper salts are copper (I) chloride, copper (I) bromide, copper (I) iodide, copper (I) cyanide, copper (II) chloride, copper (II) acetate or copper (II) stearate.

In particular preferred are copper (I) iodide and copper (I) cyanide.

Generally all alkyl or aryl phosphines are suitable. Example of phosphines employable in accordance with the present invention are triphenylphosphine and the substituted triphenylphosphines, trialkylphosphines but also diarylphosphines. One example of a suitable trialkylphosphine is tris-n-butyl phosphine. Triphenylphosphine is in view of the commercial availability preferred, in particular regarding economic issues. Generally the triphenylphosphine complexes are more stable than the trialkylphosphine complexes.

Examples of suitable complexes can be represented by the following formulae:

$[\text{Cu}(\text{PPh}_3)_3\text{X}]$, $[\text{Cu}_2\text{X}_2(\text{PPh}_3)_3]$, $[\text{Cu}(\text{PPh}_3)_4]$, $[\text{Cu}(\text{PPh}_3)_2\text{X}]$, X selected among Cl, Br, CN, SCN or 2-MBI.

Complexes which may be used in accordance with the present invention may however contain further complex ligands. Examples in this respect are Bipyridyl (for

example $\text{CuX}(\text{PPh}_3)(\text{bipy})$, X is Cl, Br or I), Biquinoline (for example $\text{CuX}(\text{PPh}_3)(\text{biquin})$, X is Cl, Br or I), and 1,10-Phenanthroline, o-Phenylenebis(dimethylarsin), 1,2-bis(diphenylphosphino)ethane and terpyridyl.

These complexes are generally diamagnetic and electrically non-conducting. They are typically colorless and are obtained as water insoluble crystals, which do melt without decomposition. In polar organic solvents, such as DMF, chloroform and hot ethanol these complexes are easily soluble. The melting points of these complexes are in the region of from 150 to 170 °C. The tetrameric copper complexes have higher melting points of from 210 to 270 °C. Preferred are copper complexes with a lower number of phosphine ligands, from the economic point of view. Preferred are therefore in particular the tetrameric complexes.

The organic halogen compound may be any organic halogen compound. In view of processing stability and for the inhibition of embrittlement due to flow out of the organic halogen compound from the stabilized polyamide composition the molecular weight of the organic composition should be selected in order to secure that the compound is not easily volatile. This selection is also preferred in view of workplace security and in view of the toxicological classification of the stabilized polyamide composition. Easily volatile organic halogen compounds furthermore do have a strong tendency to discoloration even though they satisfy the other requirements for the stabilizer.

Preferred as organic halogen compounds are in particular bromine containing compounds and/or aromatic compounds.

Generally all organic halogen compounds may be employed. Examples of suitable organic halogen compounds are aromatic compounds, such as dekabromodiphenyl, dekabromodiphenol ether, chlorinated or brominated styrene oligomers, polydibromostyrene, tetrabromobisphenyl-A, tetrakisphenyl-A derivatives, such as epoxy derivatives, such as BEB 6000 and BEG 500C, which formulas are given below, and chlorinated dimethanedibenzo(a,e)cyclooctene derivatives. Examples of

suitable aliphatic compounds are chloroparaffin, polyvinyl chloride, polyvinylidene chloride, polytetrafluoroethylene or fluoro rubber.

Suitable are furthermore organic compounds which contain further hetero atoms. Examples of such compounds are halogenated aliphatic phosphates, halogenated aromatic phosphates and halogen containing organic compounds which contain sulfur or nitrogen atoms. Examples of suitable phosphates are tris(tribromoneopentyl)phosphate (phosphate 1) and dibromodioxaphosphorine derivatives and chlorine containing polyphosphonates.

These compounds can be used singly or in combination.

If carbon-halogen-bonds are present in the complex of copper these bonds are preferably carbon-bromine bonds. In particular preferred are compounds containing TPP-Br₆ or 2-MBI-Br₂, in particular TPP-Br₆/CuJ.

Generally all phosphines and complex ligands described before are employable here, with the proviso, that the phosphines are halogenated.

The polyamide compositions in accordance with the present invention do possess significant advantages, compared with known stabilized polyamides.

The amount of copper complex, used in the stabilized polyamide compositions is not limited, as long as the mechanical properties of the polyamide are not affected detrimental. Usually the amount is between 10 and 1000 ppm copper, based on the total composition. Preferably 20 to 700, in particular 50 to 150 ppm copper are employed.

The addition amount for the halogen-containing organic compound is not particularly limited. Usually amounts are added resulting in 50 to 30,000 ppm halogen, based on the total composition. Preferred are 100 to 10,000, in particular 500 to 1500 ppm halogen.

Accordingly usually a ratio of copper to halogen in the stabilized polyamide compositions of from 1:1 to 1:3000 is obtained. Preferred is the area from 1:2 to 1:100, in particular the range from 1:5 to 1:15 (based on the molar ratio).

Higher addition amounts usually do not lead to an increase of the stabilization effect, polyamides containing more than 5% organic halogen containing compounds do have a significant lower stability. They show increased cleavage of polymer chains, which leads to premature embrittlement of the products and to strong discoloration. Preferably the content of organic halogen containing compound is less than 3 wt%, in particular less than 1 wt%.

First the thermal stability at temperatures above 150 °C is strongly increased. Furthermore, the stabilizing components are not water-soluble, accordingly also not extractable with water. Therefore, the polyamide compositions in accordance with the present invention show the advantage vis-à-vis salt containing stabilizers that they can be employed for polyamides for electric components. Since no salts, which would increase the conductivity, are present or can be brought up to the surface of the products the requirements of a high tracking resistance (CTI-value) and a high electric strength, which are satisfied by pure polyamides, also are satisfied with the polyamide compositions in accordance with the present invention.

The tracking resistance, which is determined as CTI-value is improved greatly with the compositions in accordance with the present invention. Accordingly the area of practice for the polyamide compositions in accordance with the invention is broadened to products which are used in the electro or electronic industry.

Polyamides for electrical products should possess CTI-values of 600, at least however of 550. This value is reached with pure polyamide. The CTI-value is determined in accordance with DIN-IEC 112.

When using conventional copper/halogen salt stabilizing systems failure is often accounted due to short cuts, in particular in view of the miniaturisation. Simultaneously a high embrittlement stability under prolonged thermal stress is required, requirements which could not yet be fulfilled simultaneously with a high tracking resistance in polyamides. Stabilizers on the basis of sterically hindered phenols, phosphites or amines, which do satisfy the electric requirements do not give the required long term durability. The long term durability could only be achieved with stabilizers containing KJ or KBr. Therefore, in order to achieve the desired long term thermal stability it was not possible to substitute the usual copper stabilizers, even though the requirements regarding electrical properties could not be satisfied. The polyamide compositions in accordance with the present invention do satisfy both requirements. The electrical properties of the polyamines are not altered by the addition of the stabilizing components while simultaneously the required long term thermal stability is achieved.

The stabilizing components dissolve very good during processing in the polyamide melt, therefore a good dispersion and homogeneous distribution is achieved. This simplifies the production of these polyamide compositions. At the same time the stabilizing components are compatible with all sorts of polyamines. Therefore blooming at the processing apparatuses (nozzles, extruders, molds) and the produced parts and filaments does not occur. Furthermore very good dispersion leads to improved mechanical properties, such as impact strength, compared with conventional salt stabilizers, for example CuJ, KJ, KBr.

Furthermore the polyamide compositions in accordance with the present invention do practically show no discoloration due to the stabilizing components. Therefore, it is possible to obtain polyamides colored with pigments, without color deviation. Even parts colored with TiO_2 pigments do maintain their clear white color. This opens up a further field for colored polyamides, where a higher long term thermal stability is required, which could however so long only be obtained with usual stabilizers, wherein however these have the disadvantage of their discoloration

effect. The polyamide compositions in accordance with the present invention therefore possess the advantage that they show a higher long term thermal stability compared with other stabilized polyamide compositions. Furthermore the compositions in accordance with the present invention are only lightly discolored, if at all.

For coloration of the polyamide compositions in accordance with the present invention all common pigments are suitable, such as titanium dioxide, lead white, zinc white, lipone, antimony white, carbon black, iron black, mangan black, cobalt black, antimony black, lead chromate, mangan, zinc yellow, zinc green, cadmium red, cobalt blue, berlin blue, ultramarine, mangan violet, cadmium yellow, schweinfurt green, molybdenum orange, molybdenum red, chromium orange and chromium red, iron oxide red, chromoxide green, strontium yellow, chromoxide green, molybdenum blue, chalk, ocker, umbra, green soil, terra di sienna and graphite.

A further advantage of the polyamide compositions of the present invention is the improved UV stabilization of the polyamide. The use of usual UV stabilizers, in particular of the so-called HALS stabilizers (Hindered Aminic Light Stabilizer) leads to an excellent long time stabilization of polyamides which are used outdoors under the effects of sunlight and rain, as for example, filaments for artificial lawns and door knobs or casings for side mirrors in automobiles, which could not yet be obtained with common systems. Common stabilizing systems have the drawback of the scale formation on the surface of polyamide parts during continuous weathering. This scale consists of water extractable components (salts). The polyamide compositions in accordance with the present invention do not show this drawback, no scale formation occurs. Furthermore, prolonged service life until mechanical damage of the parts is obtained. Usual stabilizer combinations of HALS-UV-compounds with antioxidants on the basis of sterically hindered phenols and organic phosphites, which are employed usually, only achieve 50% of the values found in accordance with the present invention.

The polyamide compositions in accordance with the present invention are furthermore excellent concerning their stability regarding hydrolysis. They show improved long term stability under acidic and basic conditions, vis-à-vis salt solutions, glycol water mixtures and hot fats and oils and organic solvents. Accordingly, the usually recognised decrease of mechanical strength (impact strength, tensile strength) and the tendency towards embrittlement of the polyamides is drastically reduced and the long term durability enhanced.

The polyamide compositions in accordance with the present invention can furthermore be combined without limitations with further additives, such as lubricants, plasticizers, crystallization accelerators and pigments without detrimentally effecting the desired stabilization effect. In some cases even the used additives are stabilized against thermal decomposition or discoloration in polyamides. Therefore, polyamides mixed with plasticizers, such as BBS, or with waxes, such as montanates, no longer show a high tendency to ageing, when employed in polyamide compositions in accordance with the present invention.

Polyamides containing glass bowls, fiber glass, mineral additives or other reinforcing agents furthermore show, compared with common stabilizers, a significantly improved long-term thermal ageing stability.

The polyamide compositions in accordance with the present invention show their improved stability, in particular when producing polyamide filaments. Due to the complete solubility of the stabilizing components and due to the good compatibility with the polyamide melt, high addition amounts of up to 1000 ppm copper and more are possible without processing problems. With conventional copper halogen salt stabilizers, this is not possible without blooming at the spinning nozzles, leading to the disrapture of the filaments during processing. Furthermore, scaling of copper comopunds, for example brown copper oxide, occurs at the extruder, scales which are difficult to remove and which may also lead to production problems. The polyamide compositions in accordance with the present invention do not show these drawbacks. The spinning of the polyamide melt is not effected in any way. Therefore,

it is possible to continue the production over many days, even weeks, without unwanted discontinuations. This represents a major cost factor during production.

Spinning of polyamide filaments is usually done starting from the melt. For this purpose, usually first the polyamide is melted, optionally additives are added, subsequently the melt is extruded through spinning nozzles. Following the hardening of the filaments occur due to cooling.

The production of the polyamide compositions in accordance with the present invention can usually be done by mixing at least one polyamide with at least one copper compound and at least one halogen containing organic compound, which are selected as defined in claim 1. It is possible to mix the components using common apparatuses, namely polyamide and stabilizing compounds are mixed with one another and are fused. It is preferred, however, to first fuse the polyamide and to mix in subsequently the stabilizing components. It is even more preferred to add the stabilizing compound in the form of a master batch to the molten polyamide. This simplifies in particular the metering of the stabilizing components.

Suitable mixing apparatuses are known to the person skilled in the art and comprise mixing rollers, discontinuous kneaders, continuous extruders and kneaders and static mixers. Preferred is the use of continuous extruders, single screw extruders as well as double screw extruders, which allow a good mixing. Usually the polyamide will be fused in the extruder, the stabilizing component can be metered in later through suitable openings. This process as well as the apparatuses for these purposes are known to the person skilled in the art.

It is furthermore possible to add the stabilizing components during the production of the polyamides, for example by adding them to the monomer mixture. This leads to a very good dispersion without any further mixing step which reduces the production costs and the production time.

If a master batch of the stabilizing components is used for the production of the polyamide compositions in accordance with the present invention, the master batch can be produced in discontinuous mixers which allow a very good homogenous mixing, for example a Buss-kneader. However, usually continuous mixers are used such as double screw extruders or ZSK-extruders. The matrix material employed is usually the same polyamide which will be mixed later with the master batch. It is, however, also possible to use another polyamide or another polymer.

Furthermore, the stabilized polyamide compositions in accordance with the present invention were evaluated in order to determine whether any further improvement of the discoloration tendency could be achieved. Surprisingly, it was found that a further reduction of the discoloration could be achieved by the addition of organic phosphites or inorganic phosphonates or inorganic hypophosphites. These substances are known as color stabilizers in polyamides. It was, however, also known that these color stabilizers could lead often to the formation of copper oxides with copper salts. Therefore, a grey discoloration or brown/ black discolorations occurred. Therefore, it was surprising that the combination in accordance with the present invention does not lead to any discoloration and that, furthermore, the blue discoloration, occurring sometimes after conditioning could be reduced by the addition of organic phosphites or inorganic phosphonates or inorganic hypophosphites. The slight discoloration occurring during this mixing can be cross dyed for the preparation of color stable polyamides.

It was furthermore found that this addition furthermore retards the ageing of the polyamides during thermal storage. This effect is particularly significant with organic phosphites.

The employable organic phosphites are esters of the phosphoric acid. Employable are aliphatic as well as aromatic or mixed esters. Typical examples are, for example, dimethyl and diethyl phosphite, trimethyl and triethyl phosphite as well as the additives known in the plastic processing industry. Typical examples are Tris(2,4-di-

t-butylphenyl)phosphite (Phosphite 20), Bis(2,4-di-t-butylphenyl)pentaerythritoldi-phosphite (Phosphite 21), Tetrakis(2,4-di-t-butylphenyl)4,4'-biphenyldiphosphonite (Phosphite 23), Distearylpentaerythritoldiphosphite, Diisooctylphosphite, Distearylphosphite, Triisodecylphosphite, Triisooctylphosphite, Trilaurylphosphite, Tristearylphosphite, Tris(dipropylenglycol)phosphite, Diphenylphosphite, Trisnonylphenylphosphite, Triphenylphosphite, Tris(p-nonylphenyl)phosphite. These compounds are available under the tradenames Irgafos, Alkanox and Weston from the companies Ciba, Weston and The Great Lakes. Preferred are, in particular, Phosphite 20, Phosphite 21, Phosphite 22 and Phosphite 23.

Usable inorganic phosphonates are salts of the phosphonic acid. Employable as salt builders are alkali metals, earth alkali metals and all other usual metals. Preferred are, in particular, lithium, potassium, sodium, magnesium, calcium, strontium, barium and aluminum, in particular preferred are sodium, potassium, magnesium and calcium. A preferred phosphonate is disodium hydrogen phosphonate.

The usable inorganic hydrophosphites are salts of the hypophosphoric acid. Concerning the salt building, it is referred to the above metals listed in connection with the inorganic phosphonates. The sodium salt of the hypophosphoric acid is a preferred example of the employable hypophosphites.

The addition amount of the above given additives is between 0.005 and 1.0% (50 to 10,000 ppm), preferably from 0.05 to 0.2% (500 to 2000 ppm) and in particular preferably from 0.075 to 0.15% (750 to 1500 ppm). These amounts relate everytime to the total composition.

The organic phosphites to be used are preferably meltable, processing stable and stable against extraction. This ensures that no phosphoric acid will be cleaved which may have disadvantageous effects for the total composition. The above given organic phosphites, in particular the Phosphites 20, 21, 22 and 23, satisfy the requirements excellently. Therefore, these compounds are particularly preferred.

It has, furthermore, been recognised during the preparation of the stabilized polyamide compositions in accordance with the present invention that the addition of the organic phosphite, the inorganic phosphonates and the inorganic hypophosphites should preferably occur only after the preparation of the basic composition stabilized with the stabilizing components.

If a stabilized polyamide composition in accordance with claim 1 is produced first and if the organic phosphite, the inorganic phosphonate or the inorganic hypophosphite is added only thereafter during an additional step, no discoloration occurs. The above described procedure is in particular effective with inorganic phosphonates. The organic phosphite, the inorganic phosphonate or the inorganic hypophosphite can be added as such or in the form of a masterbatch. Concerning the masterbatch technology it is referred to the previous disclosure in this respect, the same principles are valid here.

The production of the polyamide compositions is carried out usually by mixing at least one polyamide with at least one copper compound and at least one halogen containing compound, selected as defined in claim 1.

The following examples illustrate the invention.

The samples tested in the following examples have been prepared and tested as follows.

Preparation of samples

Stabilizer mixtures and Ca-stearate as lubricant are mixed with polyamide granules and melted in an extruder. The mixture is homogenized in the extruder and extruded continuously. Subsequently granules are formed. Cu concentration was always 100 ppm, halogen concentration 1000 ppm (0.1%) and Ca-stearate concentration 0.3%. After drying the granules were formed into test samples using an injection molding apparatus for measuring impact strength (DIN 53453) and bending strength (DIN 53452).

Heat ageing DIN 53497 and DIN 53446

The previously prepared test samples were put in an heat oven at 130, 150 and 165°C and were stored at these temperatures until measurements have fallen under 50% of the initial values. The period until this value was taken as halftime und is the value for the heat ageing stability of the polyamide. This value demonstrates the effect of the employed stabilizers. Since many polyamides age very rapidly without stabilization (24h at 150°C) a use of these materials without stabilization is often not possible.

Tracking resistance (CTI-values)

Test samples werde produced of a size of 3x5 cm (3mm thickness; injection molding) and tested in accordance with DIN-IEC 112.

Color determination

Discoloration of test samples was evaluated optically. In addition the color intensity was evaluated with the determination of the brightness (DIN 6174; DIN 5033, Part 1-7).

Example 1

Stabilization of PA 6 (natur), heat ageing at 150°C. Comparision with other copper stabilizers, addition amount 100 ppm copper, 1000 ppm halogen. Measurement of impact strength until value decreases to 50% of initial value (half value measurement); measurement of tracking resintance (CTI-value); color after molding and after conditioning. Samples 20 to 26 furthermore contained 1000 ppm phosphite or phosphonate.

Table 1

	Type	Compositio	Halftime (h)	CTI-value	Discoloratio	Discoloratio
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		n			n after formation	n after conditioning
1	Comparison	PA 6 (natur)	24	600	colorless	Colorless
2	Comparison	CuJ/KJ	1100	450	colorless	Light green
3	Comparison	Cu- acetate/KBr	750	400	colorless	Light blue
4	Comparison	Cu- stearate/KJ	800	450	Yellow-ish	Blue green
5	Invention	TPP-CuCN	700	600	Colorless	Colorless
6	Invention	MBI-CuCl ₂	500	600	Yellow-ish	Yellow-ish
7	Invention	TPP-CuJ/ Phosphat 1	1400	600	colorless	Almost colorless
8	Invention	TPP-CuJ/ PDBS	1200	600	colorless	Almost colorless
9	Invention	TPP-CuCN/ Phosphat 1	1400	600	colorless	Colorless
10	Invention	MBI-CuJ/ Phosphat 1	950	600	Yellow-ish	Yellow-ish
11	Invention	TPP-CuJ/ teflon wax	550	600	colorless	Colorless
12	Invention	TPP-CuJ/ TBBA-EP- Oligomer 1	1200	600	colorless	Light blue
13	Invention	MBI-CuJ/ TBBA-EP- Oligomer 2	1000	600	colorless	Light yellow
14	Invention	TPPBr ₂ - CuJ	1200	600	colorless	Light green

15	Invention	TPP-CuJ/ chloro- paraffin	1100	600	Light brown	Dark brown
16	Invention	TPP-CuJ/ Dechlorane plus	1200	600	beige	Brown
17	Invention	Cu-glycine/ Phosphate 1	950	600	beige	Beige
18	Invention	Cu-acetyl acatonate/ Phosphate 1	900	600	White grey	Green beige
19	Invention	MBI-CuCl/ Phosphate 1	1050	600	colorless	Light green
20	Invention	TPP-CuJ/ Phosphate 1/ Phosphite (20)	1100	600	colorless	Light blue
21	Invention	TPP-CuJ/ Phosphate 1/ Phosphite (21)	1200	600	colorless	Low
22	Invention	TPP-CuJ/ PDBS/ Phosphite	1100	600	colorless	Low

		(22)				
23	Invention	TPP-CuJ/ Phosphate 1/ Phosphite (23)	1150	600	colorless	Low
24	Invention	(TPP-CuJ/ Phosphate 1) in Polyamid/ Phosphite (20)	1100	500	colorless	Low
25	Invention	(TPP-CuJ/ PDBS) in Polyamid/ Phosphite (21)	1200	600	colorless	Low
26	Invention	(TPP-CuJ/ PDBS) in Polyamid/ Disodiumhy drogenphos phonate(24)	1100	550	colorless	Low

These experiments demonstrate the superior effect of the stabilizers employed in accordance with the present invention concerning tracking resistance and thermal stability.

Table 1 (cont.)

**Color determination, polyamide test samples
(CIELab-values, DIN 6174)**

after molding

after conditioning

Type	Discoloration	Brightness L-value	Discoloration	Brightness L-value	Green-red a-value	Blue-yellow b-value
1	Colorless	68.2	Colorless	69.3	-3.2	-1.8
2	Colorless	68.3	Light green	66.2	-11.7	4.2
3	Colorless	69.1	Light blue	68.2	-7.8	-1.5
4	Yellow-ish	67.5	Blue green	65.0	-7.7	2.9
5	Colorless	69.7	Colorless	69.8	-3.3	-1.5
6	Colorless	69.1	Light blue	69.9	-7.3	-3.5
7	Colorless	70.2	Yellow green	69.8	-6.3	0.2
8	Colorless	67.3	Blue green	69.3	-7.4	1.5
9	Colorless	69.8	Almost colorless	69.3	-3.5	0.6
10	Colorless	69.2	Almost colorless	71.9	-5.2	0.5
11	Colorless	69.7	Light blue	68.4	-8.8	4.0
12	Colorless	69.0	Almost colorless	69.3	-7.5	-1.2
13	Colorless	69.3	Yellow green	69.9	-6.5	3.5
14	Colorless	70.2	Light green	69.8	-9.7	4.5
16	Beige	53.17	Brown	48.54	-12.4	-8.7
17	Beige	66.94	Beige	66.39	-1.6	0.3
18	White grey	69.79	Green beige	68.39	-3.6	0.0
19	Colorless	70.63	Light green	69.04	-6.7	2.3
20	Colorless	62.13	Light blue	59.81	-3.5	-1.6
21	Colorless	63.72	Light blue	59.41	-3.4	-1.3
22	Colorless	61.86	Light blue	58.08	-3.1	-1.3
23	Colorless	64.07	Light blue	60.21	-3.7	-1.8
24	Colorless	64.68	Light blue	65.78	-4.2	-3.3

25	Colorless	65.96	Light blue	65.95	-4.4	-2.7
26	Colorless	62.89	Light blue	59.21	-3.9	-1.0

[illegible]

Example 2

Stabilization of PA 66 (natur), heat ageing test at 165°C, Compositions and measurements as in example 1

Table 2

Type	Composition	Halftime (h)	CTI-value	Discoloration after formation	Discoloration after conditioning
Comparison	PA 66 (natur)	12	600	Colorless	colorless
Comparison	CuJ/KJ	140	450	Colorless	Light green
Comparison	Cu-acetate/KBr	90	400	Colorless	Light blue
Comparison	Cu-stearate/KJ	90	450	Yellowish	Blue green
Comparison	TPP-CuJ	80	600	Colorless	Blueish
Comparison	MBI-CuJ	60	600	Colorless	Yellowish
Invention	TPP-CuJ/Phosphat 1	430	600	Colorless	Almost colorless
Invention	TPP-CuJ/PDBS	180	600	Colorless	Almost colorless
Invention	TPP-CuCN/Phosphat 1	250	600	Colorless	Colorless
Invention	MBI-CuJ/	170	600	Yellowish	Yellowish

	Phosphat 1				
Invention	TPP-CuJ/ teflon wax	110	600	colorless	Colorless
Invention	TPP-CuJ/ EP- Oligomer 1	180	600	colorless	Blue green
Invention	MBI-CuJ/ EP- Oligomer 2	180	600	colorless	Light yellow
Invention	TPPBr ₆ - CuJ	220	600	colorless	Light green
Invention	TPP-CuJ/ Viton	110	600	Colorless	colorless
Invention	TPP-CuJ/ PDBS/ Phosphite (20)	90	600	Colorless	Light blue
Invention	TPP-CuJ/ Phosphate 1/ Phosphite (21)	350	600	colorless	Light blue
Invention	TPP-CuJ/ PDBS/ Phosphite (20)	350	600	colorless	Light blue
Invention	(TPP-CuJ/ Phosphate 1) in Polyamid/ Phosphite	290	600	colorless	Light blue

	(20)				
Invention	(TPP-CuJ/ PDBS) in Polyamid/ Dinatriumh ydrogenpho sphosphate(2 4)	170	550	colorless	Light blue

As shown in example 1 the samples in accordance with the present invention do show improved tracking resistance and thermal stability

Example 3

Stabilization of PA 66, reinforced with 30% fiberglass (GF30), heat ageing test at 165°C, Measurements as in example 1. Ratios as in example 1. Halftime values relate to bending strength.

Table 3

Type	Composition	Halftime (h)	CTI-value	Discoloration after molding	Discoloration after conditioning
Comp.	PA 66 GF30	120	550	Colorless	Colorless
Comp.	CuJ/KJ	1200	450	Yellowish	Blue green
Comp.	Cu-acetate/ KBr	900	400	brown	Brown
Invention	TPP-CuJ/ Phosphat 1	1600	550	Colorless	Almost Colorless
Invention	TPP-CuJ/ teflon wax	900	550	Colorless	Colorless
Invention	TPP-CuJ/ phosphat 1/ phosphite	1300	550	Colorless	Light green

	(20)				
Invention	(TPP-CuJ/ PDBS) in polyamide/ phosphite (21)	1400	550	Colorless	Light green

Samples in accordance with the invention do show, as in examples 1 and 2 reduced tendency to discoloration.

Example 4

Stabilization of PA 66 (natur) and PA 66 GF30 with copper stabilizers, addition of 100 ppm copper, 1000 ppm halogen, 1000 ppm phosphite or phosphonate.

Measurement of initial impact strengths: Izod with PA 66 (natur) and Charpy (not notched) with PA 66 GF30

Table 4

Type	Composition	Halftime at 165°C (h)	Impact strength (kJ/m ²)
Comp.	PA 66 GF30	120	45 (Charpy)
Comp.	CuJ/KJ	1200	35 (Charpy)
Invention	TPP-CuJ/ Phosphate 1	1600	45 (Charpy)
Comp.	PA 66 (natur)	12	5.5 (Izod notched)
Comp.	CuJ/KJ	140	4.0 (Izod notched)
Invention	TPP-CuJ/ Phosphate 1	430	5.5 (Izod notched)
Invention	TPP-CuJ/ Phosphate 1/ phosphite (20)	1400	35 (Charpy)
Invention	(TPP-CuJ/ PDBS) in Polyamide/ phosphite (21)	1200	45 (Charpy)

Even mechanical properties of stabilized polyamides are improved in accordance with the present invention.

Example 5

Extraction stability of PA 6 and PA 66 GF30 with water and ethanol. Evaluation in accordance with DIN 53738. Stabilization with 100 ppm copper and 1000 ppm halogen, 1000 ppm phosphite or phosphonate. Determination of extract composition after 16h reflux.

Table 5

Type	Composition	Amount of extract (%)	Composition of extract
Comp./Water	PA 66 (natur)	0.4	Caprolactame an oligomers
Comp./Water	CuJ/KJ	0.5	As above and KJ, CuJ
Invention/Water	TPP-CuJ/ PDBS	0.3	No copper or halogen
Invention/Water	MBI-CuJ/ Phosphate 1	0.3	No copper or halogen
Comp./Water	PA66 GF30	0.3	AH salt, oligomers

Comp./Water	CuJ/KJ	0.4	As above, KJ,CuJ
Invention/Water	TPP-CuJ/ PDBS	0.2	No copper or halogen
Invention/Water	MBI-CuJ/ Phosphate 1	0.2	No copper or halogen
Comp./Ethanol	PA 6 (natur)	0.8	Caprolactame an oligomers
Comp./Ethanol	CuJ/KJ	0.9	As above and KJ, CuJ
Invention/Ethanol	TPP-CuJ/ PDBS	0.6	No copper or halogen
Invention/Ethanol	MBI-CuJ/ Phosphate 1	0.6	No copper or halogen
Comp./Ethanol	PA 66 GF30	0.6	AH salt, oligomers
Comp./Ethanol	CuJ/KJ	0.6	As above, KJ,CuJ
Invention/Ethanol	TPP-CuJ/ PDBS	0.5	No copper or halogen
Invention/Ethanol	MBI-CuJ/ Phosphate 1	0.5	No copper or halogen
Invention/Water	PA 66 (natur):TPP- CuJ/ Phosphate 1/ Phosphite (20)	0.3	No copper or halogen
Invention/Water	PA 66 GF30 : TPP- CuJ/ Phosphate 1/ Phosphite (20)	0.2	No copper or halogen
Invention/Ethanol	PA 6 (natur):TPP- CuJ/ Phosphate 1/ Phosphite (20)	0.6	No copper or halogen
Invention/Ethanol	PA 6 GF30 : TPP-	0.5	No copper or halogen

	CuJ/ Phosphate 1/ Phosphite (20)		

Samples in accordance with the present invention do show improved extraction stability, in particular no copper and/or halogen compounds are extracted. This is advantageous in view of applications in electronic parts and in the area of cosmetics, pharmaceuticals and nutrition.

Example 6

Hydrolysis stability of PA 66 GF30, decrease of mechanical properties (hardness and bending strength) after storage in 100% glycol, 48h at 135°C. 150 ppm copper, 1500 ppm halogen, 1000 ppm phosphite or phosphonate.

Table 6

Type	composition	CTI-value	Ball-pressure hardness	Bending strength	Ball-pressure hardness (aS)	Bending strength (aS)
Comp.	CuJ/KJ/ KBr	450	141	276	91	130
Invention	TPP-CuJ/ Phosphate 1	550	139	277	96	135
Invention	MBI-CuJ/ Phosphate 1	550	136	274	95	136
Invention	TPP-CuJ/ Phosphate 1 / Phosphite	550	140	278	95	135

	(20)					
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(aS): after storage, ball-pressure hardness measured in accordance with ISO 2039/1, bending strength measured in accordance with DIN 53456

Samples in accordance with the present invention do show improved tracking resistance and better mechanical properties after storage. The tests in accordance with the present invention show that with the polyamide compositions in accordance with the invention improved tracking resistance and improved long term durability can be obtained. Furthermore the lower tendency towards discoloration of the polyamide composition of the present invention is demonstrated.

Example 7

Use for the preparation of polyamide filaments (PA 6 and PA 66)

Processing: Stabilization with 60 ppm copper, 500 ppm Br due to addition of TTP-CuJ/Phosphate 1 or MBI-CuJ/PDBS. Further tests with stabilization with TPP-CuJ/Phosphate 1/Phosphite (20), 200 ppm Cu, 2000 ppm Br, 1000 ppm Phosphite.

1. No scale formation during filament formation (PA 66), no interruption during 14 days, color even without variation.
2. White colored PA 6.12 monophiles, no problems, even color.

With usual copper stabilizers every 1 or 2 days filament ruptures occur due to blooming of copper compounds (plate out).

Heat aging stabilization: Stabilization as above

Evaluation: max. decrease of 5% after 4h at 175°C (ASTM, elongation at break)

Always satisfied, with further addition of phosphite further improvement of color, further improved weatherability.

Polyamide compositions in accordance with the present invention are particularly suited for the preparation of tyre cord. Usual stabilizers are prepared with the so called ENKA process. Aqueous solutions of stabilizers are sprayed over polyamide granules, the solution penetrates and the granules are dried. One severe drawback of materials produced from these granules is the presence of water soluble copper compounds, which, in tyres, may tend to migrate into the surrounding rubber. This leads to accelerated aging of the tyre since copper acts as rubber poison, in particular concerning EPDM. This drawback does not occur with the polyamide of the invention.

Claims

1. Stabilized polyamide composition, characterized in that as stabilizer at least one copper complex and at least one organic halogen compound is contained.
2. Stabilized polyamide composition in accordance with claim 1, characterized in that the organic halogen compound is a chlorine-containing and/or bromine-containing compound.
3. Stabilized polyamide composition in accordance with claim 1 or 2, characterized in that the molar ratio copper to halogen is 1:1,5-15.
4. Stabilized polyamide composition in accordance with at least one of the preceding claims, characterized in that the at least one copper complex is a complex of a phosphine compound and/or mercaptobenzimidazole compound.
5. Use of at least one copper complex in combination with at least one organic halogen compound for the stabilization of polyamides.
6. Use in accordance with claim 5, characterized in that the at least one copper complex is a complex with a phosphine and/or mercaptobenzimidazole compound.

7. Process for the preparation of the stabilized polyamide composition, comprising the mixing of at least one copper complex and at least one organic halogen compound with at least one polyamide.
8. Process in accordance with claim 7, characterized in that the at least one copper complex and the at least one organic halogen compound are added in the form of a masterbatch.
9. Process in accordance with claim 7 or 8, characterized in that the at least one copper complex is a complex with a phosphine and/or mercaptobenzimidazole compound.
10. Stabilized polyamide composition, characterized in that as stabilizer at least one complex of copper with a phosphine compound and/or mercaptobenzimidazole compound is contained, wherein the complex possesses halogen-carbon-bonds.
11. Use of at least one copper complex with a phosphine compound and/or mercaptobenzimidazole compound for the stabilization of polyamides, wherein the complex possesses halogen-carbon-bonds.
12. Stabilized polyamide composition in accordance with at least one of the claims 1 to 4, characterized in that furthermore at least one organic phosphite, inorganic phosphonate or inorganic hypophosphite is contained.
13. Process in accordance with at least one of the claims 7 to 9, characterized in that at least one organic phosphate, inorganic phosphonate or inorganic hypophosphite is added, in a separate additional processing step to the mixture obtained in accordance with at least one of the claims 7 to 9.

Abstract

Polyamide composition, stabilized with copper complexes and organic halogen compounds

Stabilized polyamide composition, characterized in that as stabilizer at least one copper complex and at least one organic halogen compound is contained.

Docket No.

14510

Declaration and Power of Attorney For Patent Application

English Language Declaration

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

**POLYAMIDE COMPOSITION, STABILIZED WITH COPPER
COMPLEXES AND ORGANIC HALOGEN COMPOUNDS**

the specification of which

(check one)

☐ is attached hereto.

☒ was filed on October 15, 1999 as United States Application No. or PCT International
Application Number PCT/EP99/07847
and was amended on _____

(if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, Section 119(a)-(d) or Section 365(b) of any foreign application(s) for patent or inventor's certificate, or Section 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate or PCT International application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application(s)

Priority Not Claimed

<u>19847627.2</u>	<u>Germany</u>	<u>15/October/1998</u>	<input type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)	
_____	_____	_____	<input type="checkbox"/>
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TOST90-19970866

I hereby claim the benefit under 35 U.S.C. Section 119(e) of any United States provisional application(s) listed below:

_____ (Application Serial No.)	_____ (Filing Date)
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I hereby claim the benefit under 35 U. S. C. Section 120 of any United States application(s), or Section 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. Section 112, I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, C. F. R., Section 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application:

_____ (Application Serial No.)	_____ (Filing Date)	_____ (Status) (patented, pending, abandoned)
_____ (Application Serial No.)	_____ (Filing Date)	_____ (Status) (patented, pending, abandoned)
_____ (Application Serial No.)	_____ (Filing Date)	_____ (Status) (patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

09807654-061501

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